Highly crystalline poly(heptazine imides) by mechanochemical synthesis for photooxidation of various organic substrates using an intriguing electron acceptor – Elemental sulfur

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ABSTRACT

Low-defect potassium poly(heptazine imide) (PHIK-BM) was engineered for application in photocatalytic oxidation of organic substrates. Mechanochemical pretreatment of a mixture of 5-aminotetrazole in LiCl/KCl eutectics using high-energy ball milling afforded a highly homogeneous mixture that, upon sequential thermolysis at 600 °C, gave nanosized particles of PHIK–BM. The photocatalytic activity of the free-standing PHIK–BM plates was assessed in the oxidation of benzyl alcohol to benzaldehyde under visible light irradiation using elemental sulfur as an electron acceptor. Both quantitative conversion (>99%) of benzyl alcohol and selectivity (>98%) with respect to benzaldehyde were achieved. The developed method was extended to aliphatic alcohol oxidation coupled with multicomponent Hantzsch 1,4-dihydropyridine synthesis. These 1,4-dihydropyridines were also photocatalytically oxidized by PHIK–BM to the corresponding substituted pyridines, with very good yields and under mild metal-free conditions.

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1. Introduction

Photocatalysis is an attractive tool that enables chemical transformation using light as a driving force [1]. Graphitic carbon nitride (g-CN)-based polymeric semiconductors [2] are extensively studied as photocatalysts because they are able to harvest visible sunlight as an abundant energy source, the precursors for carbon nitride preparation are cheap and available, and carbon nitrides have high chemical and thermal stability [3]. g-CN has been used in the photocatalytic hydrogen evolution reaction [4], CO_2 reduction [5], oxidation of sulfides [6], and many other reactions [7], and also as a support for different catalysts [8]. Photocatalytic production of carbonyl compounds from alcohols using O_2 as an electron scavenger catalyzed by g-CN is reported in the literature as well [9,10]. According to the accepted mechanism, dioxygen receives two electrons and two protons, affording hydrogen peroxide [11]. The latter could be quite harmful for the reaction medium, as O—O bond dissociation upon irradiation leads to highly reactive hydroxyl radials [12]. These can initiate a series of undesired chemical transformations that lower the selectivity of the photocatalytic reaction.

To overcome this problem, sulfur instead of oxygen could be used as the electron scavenger, while oxidation of the alcohol would then be performed very selectively by the photogenerated holes. On the practical level this has not been explored, although sulfur is an easy-to-handle solid soluble in many organic solvents [13]. Similarly to dioxygen, sulfur can be reduced via a two-electron process in the presence of proton donors to hydrogen sulfide [14]. Unlike H_2O_2, hydrogen sulfide is a gas and can easily be removed from the reaction mixture at a slightly elevated temperature. Therefore, side reactions in which H_2S could, in principle, participate are minimized. Also, hydrogen sulfide is a valuable reagent in organic synthesis—for example, in thiophenol production [15]. Also, it can be photoelectrochemically converted in a second step to sulfur and hydrogen to close a potential catalytic cycle [16].

Recently, we reported a new carbon-nitride-based material—potassium poly(heptazine imide) (PHIK) (Fig. 1) [17]. It has the highest VB potential (+2.54 eV) within the carbon nitride family and is therefore able to oxidize water under visible light even without a co-catalyst [18]. This makes PHIK a promising candidate to explore in selective oxidation of organic substrates under visible light irradiation.

Nanocrystalline PHIK is prepared by grinding a mixture of LiCl and KCl with 5-aminotetrazole in a mortar. The product is obtained after thermolysis at 550 °C. Notably, in the UV–vis absorption spectrum a band extending up to 700 nm that corresponds to the

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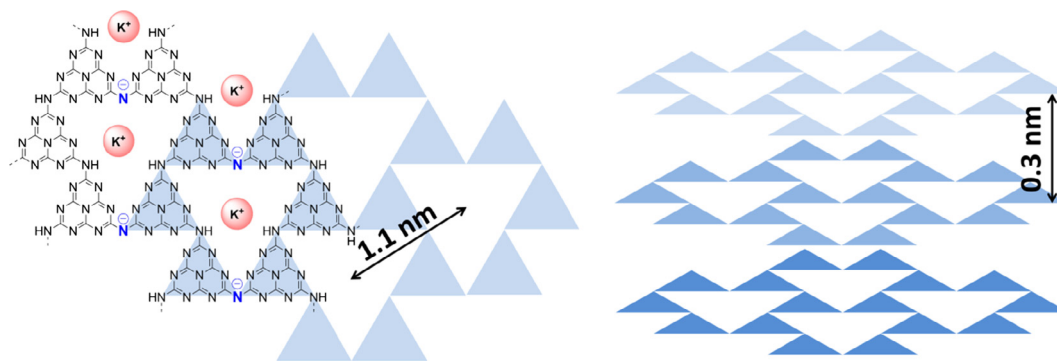E-mail address: oleksandr.savatieiev@mpikg.mpg.de (A. Savateev).

Fig. 1. PHIK structure. A holey framework of PHIK is seen in the top view (left) and a stacked structure as in g-CN in the side view (right).

photon energy ∼1.74 eV is observed [19]. This band is potentially defect-related n–π∗ transition, which, however, could play an important role in water splitting.

The specific surface area of a heterogeneous catalyst is another important parameter that influences its performance. In this view, PHIK with high surface area still remains a challenge—a material with a surface area of 50 m^2·g^{-1} has been reported so far [18]. We do not consider hard templating as a method to increase the PHIK surface area, mainly because it requires a F$^-$ source to remove the template after thermolysis [20]. In summary, an environmentally friendly method of preparing structurally ordered PHIK with a small number of defects and improved surface area is desired.

Mechanochemistry is a powerful tool that finds application in different fields of material science [21]. In view of carbon nitride chemistry, it has been already successfully used in g-CN synthesis [22]. Sample contamination with metal particles is typically unavoidable with high-energy ball milling [23]. However, it can be turned to advantage, as it was shown previously to grow thick multiwall and bamboolike carbon nanotubes [24,25]. To the extent of our knowledge, metal-particles-induced nucleation processes have not been studied for carbon nitrides. Thus, it would be intriguing to combine mechanochemistry to create nucleation seeds in situ with sequential ionothermal synthesis to obtain PHIK.

In this paper, we report on the preparation of PHIK with a small number of defects and increased surface area due to nanosized platelike morphology using a mechanochemical approach.

2. Materials and methods

Lithium chloride (≥99%) was purchased from Carl Roth; 5-aminotetrazole was purchased from Santa Cruz Biotechnology; potassium chloride (≥99.5) was purchased from Sigma Aldrich. All were used without further purification.

2.1. Characterization

^{1}H NMR spectra were recorded on a Varian 400 MHz NMR spectrometer using the chloroform residual peak (δ 7.26 ppm) as an internal standard. An Agilent 6890 network GC system coupled with an Agilent 5975 inert mass selective detector was used for reaction mixture composition analysis. Powder X-ray diffraction patterns were measured on a Bruker D8 Advance diffractometer equipped with a scintillation counter detector with CuKα radiation (λ = 0.15418 nm) applying a 2θ step size of 0.05° and a counting time of 3 s per step. FT-IR spectra were recorded on a Thermo Scientific Nicolet iD5 FT-IR spectrometer equipped with an attenuated total reflection unit at a resolution of 2 cm^{-1}. Nitrogen adsorption/desorption measurements were performed after degassing the samples at 150 °C for 20 h using a Quantachrome Quadrasorb SI-

MP porosimeter at 77.4 K. The specific surface areas were calculated by applying the Brunauer–Emmett–Teller (BET) model to adsorption isotherms for $0.05 < p/p_0 < 0.3$ using the QuadraWin 5.11 software package. Elemental analysis (EA) was accomplished as combustion analysis using a Vario Micro device. Scanning electron microscopy (SEM) images were obtained on a LEO 1550-Gemini microscope. Transmission electron microscopy (TEM) was performed on a CM200FEG (Philips) microscope operated at 200 kV. Samples were prepared by depositing a drop of a suspension of particles in ethanol on an amorphous carbon film. Optical absorbance spectra of powders were measured on a Shimadzu UV 2600 equipped with an integrating sphere. The emission spectra were recorded on an LS-50B Perkin Elmer instrument. The excitation wavelength was 350 nm. EDS investigations were conducted on a Link ISIS-300 system (Oxford Microanalysis Group) equipped with a Si(Li) detector at an energy resolution of 133 eV. Time-resolved fluorescence measurements were performed using a single-photon counting setup (TCSPC) with a Becker&Hickl PML spectrometer (modified Oriel MS-125) with a laser repetition rate of 2 MHz. The detector was a Becker&Hickl PML-16-C-1 (modified Hamamatsu) multialkaline photomultiplier. The excitation wavelength was 405 nm. Excitation was carried out using a pulsed laser diode at ∼30 nJ/cm^2 (LDH-P-C405, PicoQuant GmbH). The emission was recorded in the range 460–600 nm, while the secondary detection of the excitation pulses was blocked with a 450 nm cutoff filter. Raw decay data presented as logarithms of photon counts versus time were analyzed with PicoQuant GmbH data analysis software (Germany). The decay times were extracted by means of a reconvolution fit based on a double and triple exponential model. Considering that

$$I_{PL}(t) = \sum_{i=1}^{i=n} a_i e^{-t/\tau_i},$$

where τ_i is the lifetime and a_i is the amplitude of the ith component, the intensity-averaged fluorescence lifetime τ was calculated as

$$\langle \tau \rangle = \sum_{i=1}^{i=n} a_i \tau_i^2 / \sum_{i=1}^{i=n} a_i \tau_i.$$

A Retsch MM400 ball milling cup, Retsch 1.4112 (50 mL), and steel ball (diameter 25 mm, weight 63 g) were used to grind precursors.

2.2. LiCl/KCl eutectic synthesis

A steel ball mill cup was charged with LiCl (2.25 g) and KCl (2.75 g). A steel ball was placed in the cup and the mixture was homogenized using ball milling (20 s^{-1}, 2 min). The powder was transferred into a porcelain crucible, covered with a lid, and placed